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HIGH-ENERGY BALL MILLING ENHANCES BISPHENOL A ADSORPTION BY INCREASING SITE ACCESSIBILITY AND MODIFYING ADSORPTION ENERGETICS IN POWDERED ACTIVATED CARBON

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Abstract: The environmental persistence of the plasticizer Bisphenol-A (BPA) necessitates innovative and green adsorption solutions. High-energy ball milling (HEBM) has emerged as an effective, low-cost method for enhancing the adsorption performance of carbonaceous materials, particularly powdered activated carbon (PAC). In this study, two PACs were subjected to HEBM under identical conditions and evaluated for BPA adsorption in aqueous solution. Equilibrium data were analyzed using Langmuir, Freundlich, and Temkin isotherm models to elucidate changes in adsorption capacity and surface energetics. Ball milling increased the Langmuir maximum adsorption capacity (q_{max}), from 159.4 to 1027.0 mg/g for PAC-V_{BM} and from 305.7 to 863.6 mg/g for PAC-M_{BM}. Comparative model analysis revealed a mechanistic transition induced by HEBM. Unmilled carbons showed adsorption behavior governed by energetic heterogeneity and coverage-dependent heat variation, with the Temkin model providing the best fit. After milling, adsorption shifted toward a more site-accessible, capacity-dominated regime, with improved Langmuir representation and diminished Freundlich heterogeneity. Despite the substantial increase in capacity, affinity constants decreased, indicating that adsorption enhancement was primarily driven by increased site accessibility rather than stronger binding energy. These results demonstrate that HEBM reorganizes the distribution of effective adsorption energies, shifting BPA adsorption from an energy-controlled to an accessibility-controlled regime. The integration of multiple isotherm models offers a strong mechanistic framework for understanding structure-performance relationships in mechanically activated carbon adsorbents.

Keywords: Bisphenol A; High-energy ball milling; Powdered activated carbon; Adsorption isotherms; Site accessibility; Energy distribution.

Introduction

The presence of pollutants in water systems has become a major environmental concern due to their persistence and potential adverse effects on ecosystems and human health (Gros et al., 2017; Hernández-Abreu et al., 2021; Khan et al., 2020; Leite et al., 2023; Md Meftaul et al., 2020). Among these compounds, bisphenol A (BPA) is one of the most widely detected endocrine-disrupting chemicals in aquatic environments (Alves et al., 2023; Chaves et al., 2021; Flint et al., 2012; Sodré et al., 2010)covering dry and rainy seasons. Contaminants were extracted and concentrated using solid phase extraction (SPE. Because of its extensive use in industry, continuous release into water bodies raised significant environmental and public health concerns. Even at low concentrations, BPA has been associated with hormonal disruption, reproductive toxicity, and ecological risks (Ben-Jonathan & Hugo, 2016; Corrales et al., 2015).

Adsorption using carbonaceous materials remains one of the most effective techniques for removing organic micropollutants from water (Küçük & Önal, 2021; Onyekachukwu et al., 2025; Patil et al., 2024; Quinlivan et al., 2005)2025; Patil et al., 2024; Quinlivan et al., 2005. Powdered activated carbons (PAC) can exhibit high surface area, aromatic domains, and tunable surface chemistry, enabling strong interactions with aromatic pollutants such as BPA through π–π interactions, hydropho-

bic forces, and hydrogen bonding (Konzen et al., 2021; W. Yang & Ren, 2009). However, the adsorption performance of carbon materials is determined not only by surface area but also by the distribution of adsorption energies, pore accessibility, and surface functional groups (Gorrasi & Sorrentino, 2015; C. Li et al., 2019). The development and application of innovative adsorbents, such as modified activated carbons, are essential in enhancing BPA removal efficiency from environmental catchments.

High-energy ball milling (HEBM) has recently emerged as a promising approach for modifying carbon materials and enhancing their adsorption capacity. Ball milling is a simple, rapid, and cost-effective green technology that can facilitate the removal of various organic and inorganic pollutants (Amusat et al., 2021; Piras et al., 2019; Wu et al., 2024). Mechanical synthesis can reduce particle size to micro- and nanoscales, increase surface area, generate structural defects, expose aromatic domains, and increase pore accessibility (Ghayour et al., 2016; H. Li et al., 2024; Lyu et al., 2018) the effect of not so much discussed milling parameters such as vial to plate spinning rate, ball size distribution and type of balls on the performance (energy. These structural changes may significantly alter adsorption performance (Lapshin et al., 2021; Zhang et al., 2015). Consequently, ball-milled PAC represents a promising material for improving the efficiency of water and wastewater treatment systems in removing BPA and other organic contaminants (Bonvin et al., 2016; Fonseca et al., 2022; Huang et al., 2020; Konzen et al., 2021).

To understand how HEBM modifies and promotes adsorption benefits in carbonaceous materials, many mathematical models, known as adsorption isotherm models, can be used to provide valuable insights into the mechanisms governing adsorption processes (Sun et al., 2022; Xing et al., 2013). The Langmuir model describes monolayer adsorption onto energetically uniform sites (Langmuir, 1918), while the Freundlich model accounts for heterogeneous adsorption surfaces and multilayer interactions (Freundlich, 1907). The Temkin model considers indirect adsorbate–adsorbate interactions and assumes that the heat of adsorption decreases linearly with increasing surface coverage (Lu & Na, 2022)a long-standing challenge is how to reconcile the classical models proposed by Gibbs, Langmuir, Freundlich, and Temkin for interpreting experimentally obtained adsorption isotherms. Here, we show that the Langmuir, Freundlich, and Temkin isotherms can be derived from the Gibbs equation under different conditions for the change of surface energy (a.k.a. surface tension.

This study aims to investigate the influence of HEBM on the adsorption behavior of BPA on two PACs derived from different sources: a wood-based (vegetal) PAC and a bituminous coal (mineral) PAC. Equilibrium adsorption data were analyzed using Langmuir, Freundlich, and Temkin isotherm models to evaluate changes in adsorption capacity, surface energetics, and mechanistic regimes.

Materials and methods

Materials

Bisphenol A (BPA) was purchased from Sigma-Aldrich© (purity > 97%), and the physical and chemical properties of the BPA compound are shown in Table 1. All

solutions were prepared with ultrapure water from Mili-Q© (18.2 MΩ) at pH 7.2±2. Commercial PACs were provided by different companies: Brascarbo© for wood-based activated carbon (type: A800, Iodine number = 805 mg/g, total ash = 6.85%; particles size = 91.2% < 325 mesh; phenol index = 1.62 g/L), indicated in this study as PAC-V and the milled version as PAC-V_{BM} and, betuminous coal was purchased by Calgon-Carbon© (type: WPH-M, Iodine number = 500 mg/g (min), total ash = 8% (max); particles size = 90% < 325 mesh) and identified as PAC-M and the milled version as PAC-M_{BM}. The equipment used for milling was a Planetary Ball Mill by Tencan© with a capacity of 4 mill jars, and the balls were Zirconia Oxide stabilized with Yttrium 0.5-0.7mm supplied by Adexim Comexim®.

HEBM production

10g of each PAC was added separately to a reinforced fiber flask with a 300 mL capacity, with 50 mL of balls (density=6g/cm^3, PAC mass and balls proportion 1:30 g/g), and filled to 50 mL of ultrapure water, assuring that no more than 80% of flasks volume was filled. Both flasks were mounted on a metallic support and fixed during planetary ball milling. The milling time was set to 1 hour at 550 RPM, as suggested by Fonseca et *al.* (2022). After the milling process, the PACs (PAC-V_{BM} and PAC-M_{BM}) were removed from the flakes with a spatula, inserted into ceramic capsules, dried in a water bath and in a stove set to 100°C, then slightly macerated and sifted through a 0.07 mm sieve. After this procedure, the milled PACs were dried under vacuum for 2h and stored in an airtight glass bottle. The mass recovery for both PACs was close to 90%. Before every test, all PACs, unmilled and milled, were dried again under vacuum. The stock solution for each PAC was prepared with ultrapure water, diluted to 10 mg/ml in a flat-bottomed volumetric flask, and sonicated before testing.

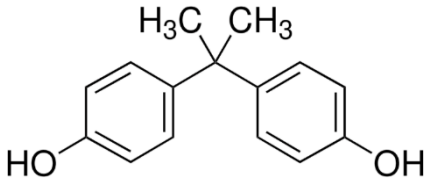
Molecular structure	
Compound	4,4-dihydroxy-2,2-diphenylpropane
Molecular formula	$(CH_3)_2C(C_6H_4OH)_2$
CAS	80-05-7
Solubility in water	300 mg/L
Molecular weight	228.29 g/mol
pKa	9.6–10.2
$LogK_{ow}$	3.4
Wavelenth	278 nm

Table 1: Physical and Chemical characteristics of Bisphenol A (BPA)

BPA Isothermal tests

BPA stock solution was prepared at a concentration of 100 mg/L in ultrapure water and stored at 4°C. Dilutions were prepared to generate the analytical curve and to achieve the planned concentrations for the isothermal study. The analytical curve was developed on a Shimadzu© UV-VIS UV-1280 spectrometer at a wavelength of 278nm, with a concentration range of 0.1-100.0 mg/L.

For the isothermal study, 100 mL of the BPA stock solution was added to Erlenmeyer flasks and diluted to BPA concentrations of 10, 20, 35, 50, 70, and 100 mg/L, with triplicate samples for each concentration. All PACs were dosed at 50 mg/L and incubated at a shaker-incubator with light protection at 150 RPM and 20±1 °C. The contact time was 24 hours.

After the contact time, the samples were filtered through a 0.45 µm membrane to remove PACs and then analyzed using a UV-Vis spectrometer. Blank experiments with BPA feed solution in the same conditions described above, but without PAC, were performed. Statistical analysis was performed in Origin® software.

Isothermal Models

Adsorption equilibrium data for BPA on PACs were analyzed using the Langmuir, Freundlich, and Temkin isotherm models to elucidate the adsorption mechanism. Each model characterizes distinct physicochemical aspects of adsorption, such as adsorption capacity, energetic heterogeneity, and adsorbate–adsorbent interactions. Integrating these models provides a mechanistic understanding of how HEBM alters the adsorption properties of PAC surfaces (Chen et al., 2022; Kamarehie et al., 2018; Üzek et al., 2022; J. Wang & Guo, 2020).

Equilibrium adsorption quantity was calculated using Eq. (1), in which C_0 and C_e are the initial and the equilibrium BPA concentrations (mg/L), respectively; V is the solution volume (L); and m is the mass of adsorbent (g).

$$q_e = \frac{(C_0 - C_e)\,V}{m} \qquad \text{(Eq.1)}$$

The following adsorption models are Langmuir (Eq.2), Freundlich (Eq. 3), and Temkin (Eq. 4 and 5):

$$q_e = \frac{q_{max}\,K_L\,C_e}{1 + K_L\,C_e} \qquad \text{(Eq.2)}$$

$$q_e = K_f C_e^{1/n} \qquad \text{(Eq.3)}$$

$$q_e = B\ln(K_m C_e) \qquad \text{(Eq. 4)}$$

$$B = \frac{RT}{b_t} \qquad \text{(Eq. 5)}$$

Where q_e (mg/g) is the amount of compound adsorbed per mass unit of activated carbon, C_e (mg/L) is the organic compound concentration at equilibrium, q_{max} (mg/g) is the maximum adsorption capacity, K_L (L/mg) is a Langmuir constant related to the affinity between the pollutant and the adsorbent, K_f (L/mg) is the Freundlich sorption constant and *1/n* is a constant related to adsorption intensity. To Temkin's model, K_m (L/g) is Temkin's equilibrium constant, B is a constant related to the heat of adsorption, R is the universal gas constant in J/(mol.K), T (K) is the temperature, and b_t

is the Temkin constant related to sorption heat in J/mol.

Results

Figure 1 presents the equilibrium adsorption behavior of bisphenol A (BPA) on vegetal and mineral carbons before and after high-energy ball milling. Experimental equilibrium data are compared with theoretical curves derived from the Langmuir, Freundlich, and Temkin isotherm models. The estimated parameters and statistical indicators are summarized in Table 2.

HEBM effect on wood-based PAC

For PAC-V (Figure 1a), all three models agree well with the experimental data, indicating that BPA adsorption occurs on a heterogeneous surface with adsorption sites of different binding energies. At low equilibrium concentrations, the adsorption capacity increases sharply. As surface coverage increases, adsorption gradually approaches saturation. The close overlap between the three model curves indicates that the system combines features of heterogeneous adsorption (Freundlich), energy variation with coverage (Temkin), and partial monolayer formation (Langmuir).

After mechanical activation, PAC-V_{BM} exhibits a markedly different adsorption profile (Figure 1b). The adsorption capacity increases significantly across the entire concentration range. Langmuir and Temkin models provide a better description of adsorption behavior than the Freundlich model, suggesting that milling reduces the surface energetic heterogeneity while simultaneously increasing the accessibility of adsorption sites. The abrupt increase in adsorption at low concentrations indicates greater availability of accessible adsorption domains.

The Langmuir model indicates that q_{max} increased from 159.36 to 1026.97 mg/g, indicating a more than sixfold enhancement after milling. This substantial increase suggests that mechanical activation significantly improved the accessibility of adsorption sites, likely through particle-size reduction, thereby increasing the specific surface area and exposing previously inaccessible micropores. However, the Langmuir affinity constant (K_L) decreased from 0.150 to 0.028 L/mg, indicating a reduction in average adsorption strength per site after milling. This trend demonstrates that the improvement in adsorption performance can be primarily driven by an increase in the number of available sites rather than by intrinsic binding energy.

The Freundlich model further supports this interpretation. The heterogeneity parameter (*1/n*) increased from 0.228 to 0.472, indicating reduced surface heterogeneity after milling. This suggests that mechanical activation exposed a larger number of adsorption sites with more uniform energetic characteristics. At the same time, the decrease in the quality of the Freundlich model fit (R^2 from 0.975 to 0.842) indicates that adsorption behavior became less influenced by heterogeneous energy distributions.

The Temkin model provided an excellent fit to the sample PAC-V, with R^2 = 0.992 and a low reduced chi-square value (χ^2 = 25.68), indicating the best statistical performance among the three tested isotherm models. Therefore, adsorption on PAC-V is influenced by progressive changes in energy as sites are occupied. After milling (PAC-V_{BM}), the Temkin constant *B* increased significantly (from 26.78 to 224.21),

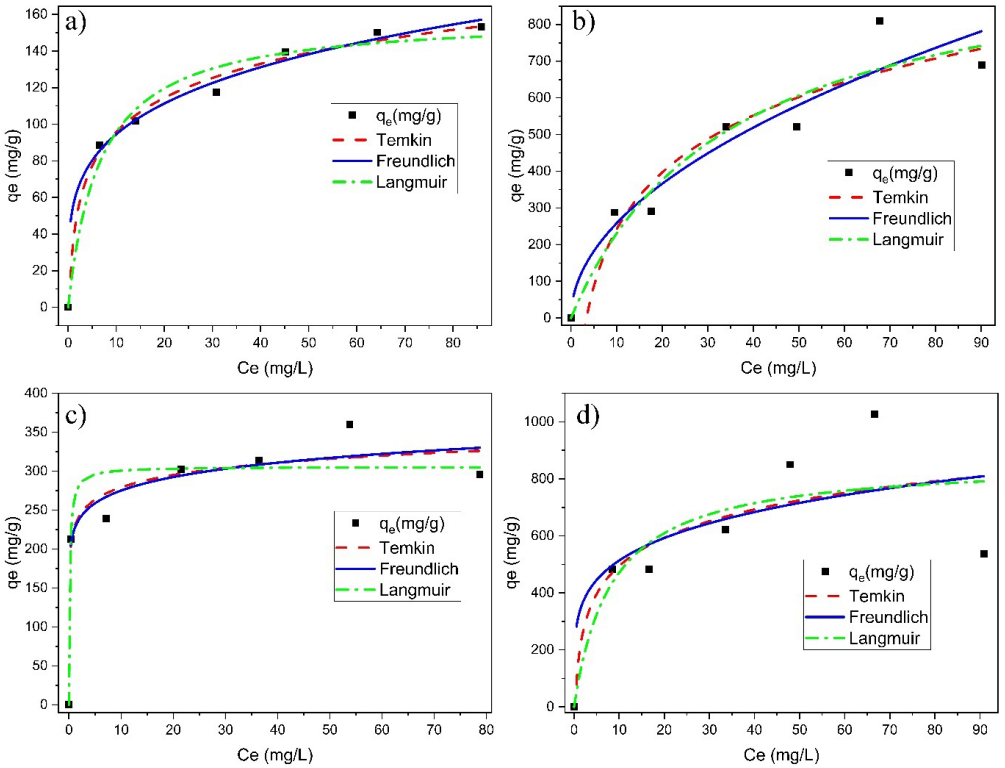


Fig. 1: Isothermal curves for Langmuir, Freundlich, and Temkin adsorption models: a) PAC-V; b) PAC--V_{BM}; c) PAC-M; d) PAC-M_{BM}.

Isotherm Models	Parameters	V	V_{BM}	M	M_{BM}
Langmuir	q_{max}	159.36 ± 7.65	1026.97 ± 207	305.68 ± 17.17	863.64 ± 174
	K_L	0.150 ± 0.035	0.028 ± 0.01	6.005 ± 3.55	0.119 ± 0.11
	R^2	0.978	0.924	0.919	0.745
	χ^2	75.32	6828.32	1372.36	32169.77
Freundlich	K_f	56.40 ± 4.19	91.40 ± 44.21	224.56 ± 23.01	319.32 ± 212
	1/n	0.228 ± 0.02	0.472 ± 0.12	0.088 ± 0.03	0.206 ± 0.17
	R^2	0.975	0.842	0.732	0.299
	χ^2	21.84	8630.98	955.67	43856.26
Temkin	*B*	26.78 ± 2.32	224.21 ± 45.17	22.72 ± 6.31	142.76 ± 92.8
	K_m	3.585 ± 1.48	0.293 ± 0.14	21689 ± 77107	3.194 ± 9.86
	R^2	0.992	0.918	0.953	0.731
	χ^2	25.68	7376.67	794.91	33986.11

Table 2: Isotherm models and the parameters obtained for all PACs

suggesting a broader distribution of adsorption energies with coverage increase. However, the derived apparent energy parameter decreases, confirming that newly exposed sites possess lower average binding energy.

HEBM effect over bituminous coal PAC

A similar, but mechanistically more complex, trend is observed for mineral carbon before (PAC-M) and after milling (PAC-M_{BM}). For PAC-M (Figure 1c), the adsorption capacity is initially higher than that observed for PAC-V. The isotherm curves show rapid adsorption at low equilibrium concentrations followed by a gradual approach toward saturation. In this system, the Langmuir model captures the early adsorption behavior reasonably well, suggesting that adsorption occurs on relatively well-defined sites. However, the continued increase in adsorption capacity at higher concentrations indicates the presence of energetic heterogeneity, consistent with the predictions of the Freundlich and Temkin models.

The effect of HEBM on PAC-M_{BM} is shown in Figure 1d. Similar to the wood-based carbon system, ball milling substantially increases the adsorption capacity, confirming that mechanical activation improves the accessibility of adsorption sites. However, the experimental data points are more dispersed for this system, suggesting that milling introduces structural disorder and heterogeneous defect sites. In this case, both the Freundlich and Temkin models provide reasonable descriptions of the adsorption behavior, while the Langmuir model slightly underestimates adsorption at intermediate concentrations.

The Langmuir model shows a substantial increase in qmax from 305.68 to 863.64 mg/g, confirming that HEBM also enhances the availability of adsorption sites in bituminous coal mineral carbon. However, the quality of the Langmuir fit decreases (R^2 from 0.919 to 0.745), indicating that adsorption becomes less consistent with ideal monolayer assumptions after milling. Additionally, the affinity constant (K_L) decreases, further supporting the conclusion that adsorption enhancement is driven by increased accessibility rather than stronger interactions.

The Freundlich model shows a substantial deterioration in fit quality, with R^2 decreasing from 0.732 to 0.299, indicating that the adsorption behavior of PAC-M_{BM} cannot be adequately described by a simple heterogeneous adsorption model. Although the Freundlich constant K_f increases substantially, the high parameter uncertainty suggests that the surface becomes structurally and energetically more complex after milling.

The Temkin model remains the most representative for the unmilled mineral carbon (R^2 = 0.953), showing that adsorption is governed by a progressive decrease in adsorption heat with increasing coverage. The higher value of *B* in PAC-M indicates the strongest apparent energetic interactions among the four materials. This may be associated with the presence of more organized aromatic domains or specific high-energy adsorption sites. However, for PAC-M_{BM}, the quality of the Temkin fit decreases (R^2 = 0.731), and the associated parameters exhibit high uncertainty. Although the adsorption capacity increases, the estimated average energy decreases, reinforcing the idea that mechanical activation promotes

an adsorption regime more dominated by structural accessibility. This suggests that mechanical activation introduces significant structural disorder and a broader spectrum of adsorption environments.

Discussion

Adsorption is a physicochemical phenomenon that is important in both natural and engineering processes (Calisto et al., 2015; Diniz et al., 2023; Mailler et al., 2016) oxazepam, sulfamethoxazole, piroxicam, cetirizine, venlafaxine and paroxetine. In studying adsorption equilibrium, a long-standing challenge is reconciling the classical models proposed by Langmuir, Freundlich, and Temkin for interpreting experimentally obtained adsorption isotherms (Lu & Na, 2022). Fitting experimental adsorption data to an appropriate isotherm model is crucial for understanding the adsorption mechanism in a system and predicting its behavior (Kalam et al., 2021).

PAC is known for its strong ability to selectively adsorb a wide range of pollutants, including BPA, even in the presence of heavy metals and natural organic matter, demonstrating excellent performance in both synthetic and real water samples. (Chen et al., 2022; Hakimabadi et al., 2025; Hernández-Abreu et al., 2020) As shown in Table 3, HEBM is a reliable and efficient option for synthesizing carbonaceous materials across various primary sources and adsorbates. The milling effect can increase adsorption by a factor of 1.3 to 23, as illustrated in Table 3. In this work, consistent improvement is observed for both PACs, as reported in the literature, and they exhibit high BPA adsorption capacities.

Mechanistic studies showed that ball milling improves adsorption through multiple simultaneous pathways, including increased oxygen-containing functional groups (carboxyl, lactonic, hydroxyl) (Gao et al., 2024; Kim et al., 2012; Zhuang et al., 2021), exposed graphitic structures that facilitate cation-π interactions, increase aromaticity and hydrophobicity, and reduce particle size (Gorrasi & Sorrentino, 2015; Qanytah et al., 2020). Notably, surface area changes showed context-dependent patterns despite a reduction in surface area, indicating that surface chemistry modifications can outweigh surface area expansion. (Biener et al., 2009; Wu et al., 2024). These structural changes are exactly the modifications expected to change the effective energy landscape experienced by adsorbates in water.

In both wood-based (vegetal) and bituminous coal (mineral) PACs, HEBM significantly increases adsorption capacity, confirming that structural accessibility is a dominant factor in BPA adsorption. However, the impact on surface energetics differs between the two materials. This transition provides strong evidence that HEBM modifies not only the structural properties of activated carbon but also the effective adsorption energy landscape, redefining the dominant factors governing adsorption performance (Shen et al., 1996; Yuan et al., 2023).

For wood-based PAC, milling leads to a more uniform and accessible adsorption landscape, shifting the mechanism toward Langmuir-type behavior. In contrast, bituminous coal carbon exhibits increased energetic and structural disorder after milling, resulting in poorer model fits and more complex adsorption behavior. Despite these differences, both systems show that adsorp-

Reference	Source	Adsorbate	Adsorption Capacity (mg/g)		Increasing Capacity
			Unmilled	Ball-milled	
This work	bituminous coal	Bisphenol A	305.68	863.64	2.83×
	wood-based	Bisphenol A	159.36	1026.97	6.44×
(Wu et al., 2024)	Hydrochar (220°C)	Norfloxacin	24.29	68.53	2.82×
(Nasrullah et al., 2021)	Activated carbon	Methylene blue	227.14	298.27	1.31×
(Xu et al., 2021)	Biochar	Reactive red	1.70-3.60	9.20-34.8	5.4×
(Xiang et al., 2020)	Wheat stalk biochar	Tetracycline	21.67-28.64 mg/g	84.54 mg/g	3×
(Wei et al., 2020) copper oxide (CuO	Biochar	Reactive Red 120	20% removal	46% removal (57.59 mg/g)	2.3×
(X. Yang et al., 2022)	Biochar	Titan Yellow	8.1 mg/g	182.3 mg/g	23×

Table 3: Reported adsorption capacity of various carbonaceous milled sources

tion shifts from an energy-controlled regime in unmilled carbons to an accessibility-controlled regime after mechanical activation (Lamberti et al., 2024 .

These observations support the hypothesis that HEBM reshapes the energetics of activated carbon surfaces, exposing previously inaccessible adsorption domains while simultaneously modifying the distribution of adsorption energies (Eguchi et al., 2020; Nan et al., 2024; Wannasen et al., 2022). As a result, adsorption transitions from an energy-controlled regime to an accessibility-controlled regime (Qiu et al., 2020; Y. Wang et al., 2024; Yuan et al., 2023) chitosan physicochemical transformations that occur during high energy ball milling are investigated and correlated with adsorption capacity of organic pollutants (using azo-dye reactive red 2 as molecular probe. BPA molecules initially occupy high-energy adsorption sites, likely associated with graphitic edge defects or oxygen-containing functional groups that can form strong interactions with aromatic molecules (D. Yang et al., 2021).

The Freundlich parameters further corroborate this interpretation. Relatively low values of the heterogeneity parameter *1/n* indicate pronounced surface heterogeneity and a broad distribution of adsorption energies (Jin et al., 2014).

Although the Langmuir model is less representative for unmilled carbons, it provides valuable information regarding adsorption capacity. For unmilled samples, moderate Langmuir capacities suggest that only a portion of the potential adsorption sites is accessible at equilibrium (Srivastava & Goyal, 2010; Zangi, 2024). Ball milling increases the Langmuir adsorption capacity of both ball-milled PACs, thereby increasing the number of accessible adsorption sites (Harindintwali et al., 2023). The increase in q_{max} is pronounced for PAC-V_{BM}, suggesting that mechanical activation effectively exposes previously inaccessible microporous domains inside the carbon structure.

Simultaneously, the Freundlich heterogeneity parameter increases, indicating reduced apparent energetic heterogeneity. This finding suggests that the HEBM technique partially homogenizes accessible adsorption sites by exposing internal carbon surfaces with similar adsorption characteristics (Gao et al., 2024; Lv et al., 2026).

The Temkin analysis shows that the apparent adsorption energy decreases after milling, despite an increase in adsorption capacity. This result indicates that enhanced adsorption performance arises from greater accessibility of adsorption sites rather than stronger intrinsic adsorbate–adsorbent interactions (Takaesu et al., 2019; Wu et al., 2024).

To thoroughly assess whether ball milling alters the adsorption energy landscape and improves site accessibility, future research should systematically vary ball-milling parameters, analyze changes in energy distributions, and clarify kinetic mechanisms. Although the present study focused on adsorption equilibrium and isotherm analysis, a discussion of adsorption kinetics is also suggested, as the rate at which BPA is removed from solution is an important practical consideration for water treatment applications. Future work should include detailed kinetic studies to further elucidate the impact of mechanical activation on adsorption rates and mechanisms.

Conclusions

This study shows that HEBM significantly affects both the adsorption capacity and the mechanistic behavior of carbon-based adsorbents used for BPA removal. A comparison of Langmuir, Freundlich, and Temkin models indicates that high-energy ball milling fundamentally changes both the adsorption capacity and the mechanistic processes governing BPA uptake on biomass-vegetal and mineral carbons.

Despite the significant increase in adsorption capacity, the decline in the Langmuir affinity constants and the Temkin apparent energy parameters indicates that the improvement in adsorption does not stem from stronger interactions between the adsorbate and the adsorbent. Instead, the results consistently demonstrate that HEBM enhances adsorption mainly by increasing the accessibility of adsorption sites. The combined analysis of Langmuir, Freundlich, and Temkin models revealed a distinct mechanistic shift. Unmilled carbons displayed adsorption behavior driven by energetic heterogeneity and coverage-dependent heat variation, while ball-milled carbons showed adsorption increasingly governed by site accessibility and adsorption capacity.

This transition was more pronounced for PAC-V_{BM}, which became a more accessible and relatively uniform adsorption system, whereas PAC-M_{BM} showed increased structural complexity after milling. These differences emphasize how the precursor structure affects the response to mechanical activation.

Overall, HEBM reorganizes the distribution of effective adsorption energies, shifting BPA adsorption from an energy-controlled to an accessibility-controlled regime. These results provide important insights into the structure–energetics–performance relationship in carbon-based adsorbents and support the use of mechanical synthesis as a strategy to improve the removal of emerging pollutants from water systems.

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